Impact of Alternative Fuels on Gas Turbine and Diesel Engine Combustion

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Office of Naval Research
Dr. Dave Shifler, Program Manager
Assess fuel impact on gas turbine engine performance

- Alternate Fuel: Phys & Chem Prop
- Surrogate for alternate fuel

Detailed Kinetics for Surrogate

Selection of physics-based tools sets

Simulations

Probable impact on combustor

Interpretations and Engine Impact

From Med Colket, UTRC
Examine effects of alternative fuel (F-T and biofuels) on diesel engine combustion

- Navy has many diesel engines
- With Jim Cowart and Patrick Caton, U.S. Naval Academy

Naval Academy Cooperative Fuels Research (CFR) diesel test engine
Navy is interested in Fischer-Tropsch (FT) fuels: They can contain large amounts of singly-methylated iso-alkanes.

**FT analysis (NIST*)**
- 57% single methyl branch alkanes
- 25% n-alkanes
- 16% multiple branched alkanes
- 2% cycloalkanes

*Smith et al. Int. J. Propulsion (2008)*
We are first focusing on 2-methyl alkanes have a single methyl branch and interesting ignition behavior.

<table>
<thead>
<tr>
<th>Species</th>
<th>Cetane No.</th>
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<tbody>
<tr>
<td>nC₇H₁₆</td>
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</tr>
<tr>
<td>C₇H₁₆₋₂</td>
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<tr>
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<tr>
<td>C₉H₂₀₋₂</td>
<td>54</td>
</tr>
</tbody>
</table>
Chemical Kinetic Mechanism for 2-methyl alkanes

Includes all 2-methyl alkanes up to C20 which covers the entire distillation range for gasoline, jet and diesel fuels.

Built with the same reaction rate rules as our successful iso-octane and iso-cetane mechanisms.

7,900 species
27,000 reactions
Why do we need to get the distillation curve right for diesel combustion?

6-component diesel surrogate

diesel spray calculation

Light components come off first near the upstream portion of the diesel jet

**Experimental Validation**

- Idealized chemically reacting flow systems with/without simplified transport phenomenon

Jet Stirred Reactors

Premixed Laminar Flames

Shock tube

Non Premixed Flames

Combustion Parameters
- Temperature
- Pressure
- Mixture fraction (air-fuel ratio)

Mixing of fuel and air

Engine Combustion

High pressure flow reactors

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2-methylhexane comparison in the RCM

Experimental data:


Stoichiometric/’air’ mixtures 15 atm

Entire compression stroke simulated and heat loss simulated after end of compression

Ignition Delay Time (ms)

Temperature at End of Compression (K)

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2-methyl heptane model behaves well under high temperature shock tube conditions

\[ \phi = 3, \ P = 21 \ atm, \ 1.355\% \ fuel, \ O_2/Ar \]

Experiments: Dayton high pressure shock tube
Previously shown that simulated ignition behavior of n-alkanes showed little dependence with carbon length.

Westbrook et al. Comb. Flame 2009

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2-methyl alkanes show effect of chain length at higher equivalence ratio and pressure (Dayton conditions):

\[ \phi = 3, P = 21 \text{ atm}, 1.355\% \text{ fuel, } O_2/Ar \]

Reactivity increases with chain length:

- Biggest fuel effect of chain length found in NTC region.
2-methylalkanes show less NTC than n-alkanes

\( \phi = 3, \ P = 21 \ \text{atm}, \ 1.355\% \ \text{fuel}, \ \text{O}_2/\text{Ar} \)

Less NTC behavior in 2-methylalkane

- 2-methylalkane less reactive than n-alkane

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Comparison of reactivity for all the n-alkanes and 2-methyl alkanes

(\(\phi = 3\), \(P = 21\) atm, 1.355% fuel, \(O_2/Ar\))

Reactivity increases with chain length

Effect of chain length for n-alkanes now observed
Opposed-flow Diffusion Flame (OPPDIF) comparisons for a 2-methyl heptane

- The one dimensional flame structure is ideal for modeling.
- The emissions and temperature profiles are dependent on chemical kinetics due to the non-turbulent flame.

Port diameter = 25.4 mm
Port Gap = 20 mm
Overall good prediction of major and minor species of 2-methylheptane

**Good prediction of major species profiles**

**Important minor species are well predicted**
Further experimental validations planned, 2-methylheptane

- Counterflow Flame Ignition/Extinction
  UC San Diego
- Jet Stirred Reactor
  CNRS Orleans, France
- Shock Tube
  Rensselaer Polytechnic Institute, New York
- Ignition Quality Tester (IQT)
  NREL, Colorado
- Flow Reactor
  Princeton University, New Jersey
Collaborating with the Naval Academy on fuel effects in diesel engine

Mixtures of n-hexadecane and toluene (mixtures are by liquid volume) (Midshipman Aaron Carr)

Experiments on n-hexadecane/toluene mixtures in a Diesel CRF engine (SAE 2010-01-2188: Mathes, Ries, Caton, Cowart, Prak, Hamilton, US Naval Academy)

Ignition delay is defined from start of injection to 10% mass burned

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Summary for LLNL work

A new chemical kinetic mechanism for 2-methyl alkanes has been developed:

• The mechanism covers the entire distillation curve of practical gasoline, jet and diesel fuels (C₇-C₂₀).
• The model successfully reproduces the experimental data currently available for this class of fuels.
• Further validations planned.
• Key differences between 2-methylalkanes and \textit{n}-alkanes are reproduced by the model.
Detailed Modeling of Low-Temperature Alkane Oxidation:
High-Pressure Rate Rules for Alkyl+O₂ Reactions

Hans-Heinrich Carstensen, Lam K. Huynh, Stephanie M. Villano, and Anthony M. Dean

Chemical Engineering Dept.
Colorado School of Mines

Third Fuels Summit
September 20-23, 2010
Development of large detailed chemical models facilitated by the use of rate estimation techniques

- Typical hydrocarbon gas phase reaction mechanisms contain
  - Hundreds of species
  - Thousands of reactions, many pressure-dependent

- Problem: How to assure consistency in rate constant assignments?
  - Experimental info only available for small fraction of reactions
  - Often literature data over limited range of conditions
  - High level calculations restricted to small molecules

- Solution: Develop accurate rate constant estimation method
  - Use high-level theory to calculate rate constants for smaller species
  - Generalize results on a per-site basis and use these for larger species
  - Use rate rule based rate constants as input for pressure-dependence analysis
Model development: from electronic structure calculations to pressure-dependent rate constants

- Gaussian Software®
- Geometry, Frequencies, Electronic Energy, Dipole Moment, Polarizability, …
- FANCY
- Heat of Formation, Entropy, Heat Capacity
- TSTdG
- 3-Freq Representation, NASA Polynomials
- CHEMDIS
- High-pressure Rate Constants $k_\infty(T)$ for Elementary Reactions
- Pressure-dependent Rate Constants $k(T,P)$ for Apparent Reactions

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Reaction classes analyzed

- H and CH$_3$ Abstraction from Alkanes, Cycloalkanes, Alkenes

- Intramolecular H-Abstraction
  *The Kinetics of Pressure-Dependent Reactions*, in Comprehensive Chemical Kinetics (Elsevier), 2007, 42 105-187

- H and CH$_3$ Abstraction from Alcohols, Elimination of Water from Alcohols

- RO$_2$ Isomerizations
- RO$_2$ Concerted Elimination of HO$_2$
- QOOH = Cyclic Ether + OH
- O$_2$QOOH Isomerization
- O$_2$QOOH Concerted Elimination of HO$_2$
Alkyl isomerizations consistent with expectations

Primary to secondary H- atom shift reactions:

- Lower activation energy for 5 and 6-member ring TSs with less ring strain
- Lower A-factor as more CH2 rotors tied up in TS
- Additional calculations ongoing to confirm consistent behavior
  - Results used as basis for rate rules
N-propyl + O2 chemistry: Fast isomerization of CCCOO• adduct leads to chain branching

- Only important pathways for n-propyl + O2 are isomerization, concerted elimination and redissociation
**i-propyl+O2: Slower isomerization of CC(OO•)C adduct leads to chain inhibition**

- Concerted elimination dominant for isopropyl + O₂
  - branching pathway inhibited
- Detailed calculations show other pathways can be neglected
RO$_2$ isomerizations show same qualitative behavior as alkyl radicals

- Activation energy depends on ring size and overall thermochemistry
- Again amenable to rule generation
Comparison of model predictions to propane ignition over the NTC region in a RCM

- Expect all predictions to be faster than data
  - Predictions adiabatic
  - Expect heat loss at longer times in data
- All models capture NTC behavior
  - NTC region at higher T with CSM model
  - Reduced CSM model, with much smaller reaction subsets for both RO2 and O2QOOH, very similar to full model
- Analysis suggests substantial differences in Galway and CSM models
  - Galway model* uses LLNL rate rules

Experimental data from Galway RCM:
Significant differences in CSM vs. LLNL rate constants (e.g. RO2 isomerization)

- CBS-QB3 results generally lower than LLNL values for 5-member TS
- CBS-QB3 results much higher than LLNL values for 6-member TS
  - Mainly due to higher A-factors (much higher than alkyl isomerizations)
- Differences lead to significantly different reaction pathways
Summary/Next Steps

- Mechanism constructed with rate constants based on unadjusted CBS-QB3 potential energy surfaces captures NTC behavior in propane oxidation
  - Need to extend mechanism to larger systems where more data available to reach firm conclusions on its success
- Relatively few reactions of RO₂ found to be important for ignition calculations
  - Significantly simplifies accounting for effects of pressure on reaction rates and branching ratios
- Extension to larger systems facilitated by ability to generalize results into reaction rate rules
- Extend approach to consider second addition of O₂ (to QOOH) that leads to low temperature chain branching